

Investigation of liquid/solid interfaces over macroscopic distances using X-ray photoelectron spectroscopy

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X-ray photoelectron spectroscopy (XPS) serves as a powerful tool for investigation of surfaces and interfaces in a wide variety of fields. Composition and bonding environments within these thin layers are crucial in the investigation of e.g. electrochemical or catalytic processes. While complex setups have been successfully applied to investigate liquids in ultra-high vacuum (UHV) environments [1,2], ionic liquids (IL) have been widely utilised for XPS studies as their negligible vapour pressure allows for stable measurement conditions in UHV [3,4]. Foelske-Schmitz et al. investigated charging phenomena during XPS measurements on ionic liquids and suggested that high surface area carbon supports may allow for determination of reliable binding energies (BE) without charging due to the high double layer capacitance of the support [5]. Subsequent measurements further confirmed that the electrochemical double layer formed at the substrate/IL interface has to be considered when irradiating/measuring at the IL/UHV interface [6, 7, 8]. It is well established that the open circuit potential (OCP) reflects the potential difference between the bulk of an electrode and an electrolyte. The potential difference between both phases is constant as long as the interface is in dynamic equilibrium.

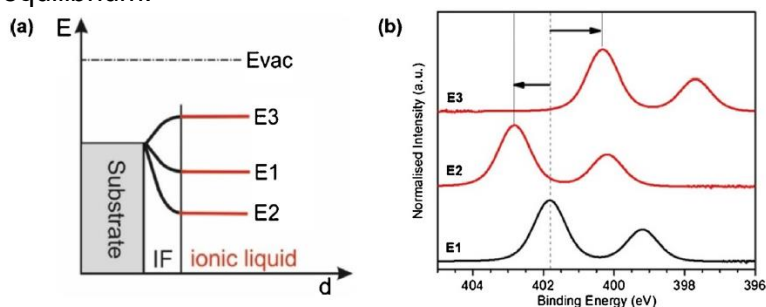


Figure 1: a) Energy scheme explaining the differences of BE by different potential drops within the double layer at the ionic liquid/substrate interface (IF). E3 corresponds to lower BE whereas E2 corresponds to higher BE; b) Schematic representation of N 1s XPS.

Conversely, BE measurements may allow for determination of the OCP in one half-cell (Fig. 1). While no significant X-ray induced charging could be observed using a monochromatic X-ray source, BEs were found to vary by 0.4 eV among the used substrates. Flood gun experiments showed a large shift of BE of IL prepared on semiconductor materials towards lower values, while on metallic supports this shift was significantly smaller, thus further confirming that the substrate/IL

interface determines the BE values measured at the IL/UHV interface [8]. We have subsequently varied the dopant and dose in semiconductor substrates to assess influence of the charge carrier density and mobility on the measured BE. Furthermore, the effects of exchanging the cation/anion as well as influence of the IL viscosity and different preparation processes will be presented and discussed.

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